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FACULTY OF **ENGINEERING AND ARCHITECTURE**

A NEW METHOD FOR THE MEASUREMENT OF THE BACKBITING RATE COEFFICIENT IN ACRYLATE RADICAL POLYMERIZATION

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Introduction

Pulsed laser polymerization has emerged as the leading technique for the determination of the **propagation** rate coefficient k_p.[1] In the PLP-SEC trace, inflection points (L_j; j = 1, 2, …) are identified that are directly linked to k_p via:

$$L_j = k_p\,[M]_0\,(j\Delta t\,)$$

For systems with several radical types, the obtained k_p must be seen as an apparent averaged one ($k_{p,app}$). For example, in acrylate radical polymerization both end-chain radicals (ECRs; $k_{p,ecr}$) and mid-chain radicals (MCRs; $k_{p,mcr}$) can be present.[2,3] The tendency of ECRs to switch to MCRs is expressed by the **backbiting** rate coefficient k_{bb}.

In the present work, a **new and accurate method** is presented to determine k_{bb} from inflection point PLP-SEC data.

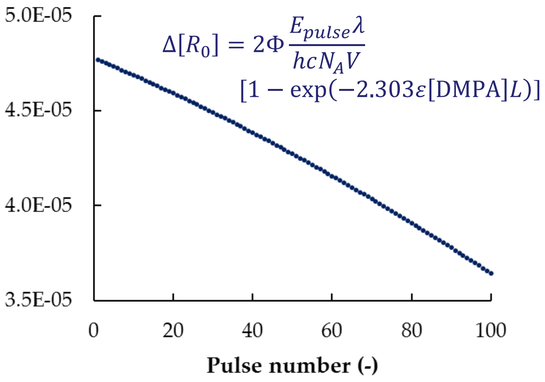
Working principle of the new method

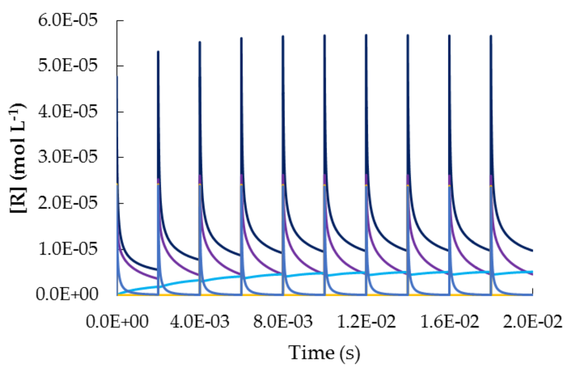
- Variation of the **solvent volume fraction** (Φ_S=0-0.75)
  → Independent change of the average MCR lifetime
  → Increased sensitivity toward k_{bb}
- Regression analysis using a detailed **kinetic Monte Carlo** model to inflection point data in the low frequency range

	Equation	Bulk (Φ_S = 0)	Solution (Φ_S = 0.75)
Dark time [s]	$\frac{1}{\nu}$	10^{-2}	10^{-2}
Average lifetime ECR [s]	$\frac{1}{k_{bb}}$	10^{-3}	10^{-3}
Average lifetime MCR [s]	$\frac{1}{k_{p,mcr}(1-\Phi_S)[M]_{0,bulk}}$	1.4 10^{-3}	5.7 10^{-3}

Kinetic Monte Carlo modeling for the simulation of the entire PLP-SEC trace

Explicit calculation of the time dependence of the radical concentration

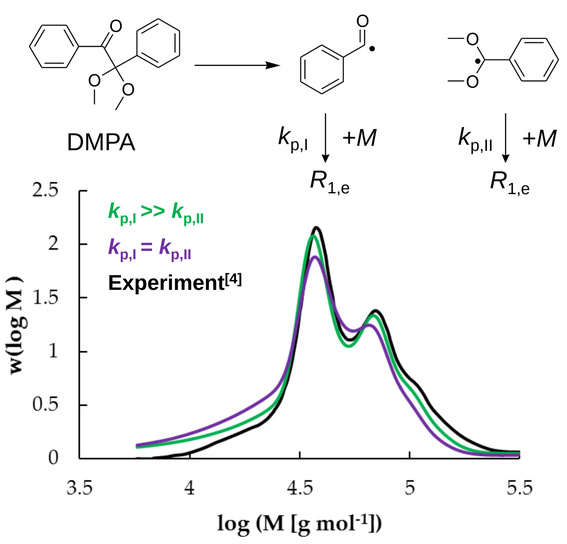




E_{pulse} = 2.5 mJ, λ = 351 nm, [DMPA] = 5 mmol L^{-1}
Φ = 0.8, ε = 280 L mol^{-1} cm^{-1}, V = 0.2 mL, L = 5.2 mm

Focus at 0 < t < 0.02 s (first 10 dark periods)

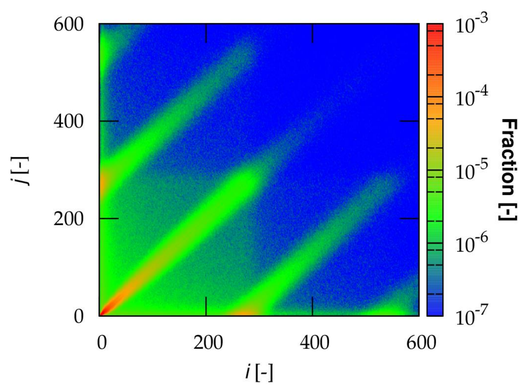
Differentiation in chain initiation capability



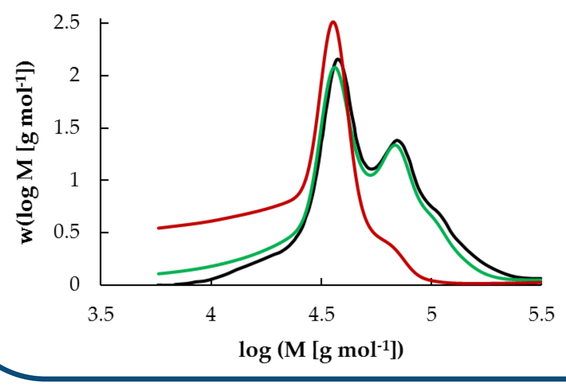
Importance of short-long termination

Visualization of termination reactions

$R_i + R_j \rightarrow P_{i+j}$



Validation of the composite k_t-model



Composite model

$$i \le i_c\text{: } k_t^{app}(i,i) = k_t^{app}(1,1)i^{-\alpha_S}$$
$$i > i_c\text{: } k_t^{app}(i,i) = k_t^{app}(1,1)i_c^{-\alpha_S+\alpha_L}i^{-\alpha_L}$$

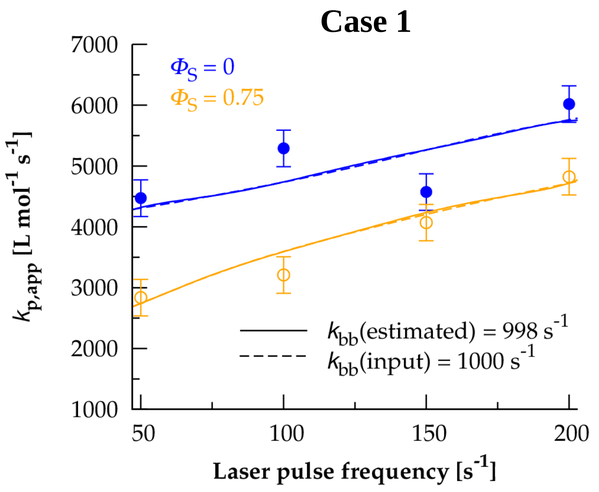
Simple power law model

$$k_t^{app}(i,i) = k_t^{app}(1,1)i^{-\alpha}$$

Experiment[4]: PLP of *n*-butyl acrylate with DMPA as photoinitiator; frequency: 500 s^{-1}

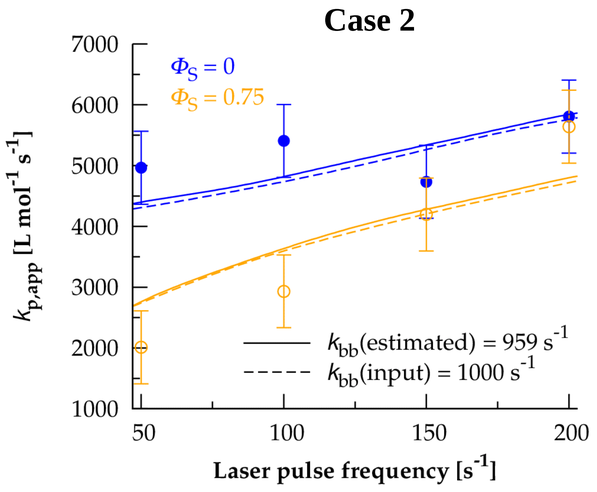
In silico validation of the new method

In silico experiment: $k_{p,app} = \hat{k}_{p,app}\left(k_{bb}^{input}\right) + e(\sigma)$ with $e(\sigma)$ a standard normally distributed error



σ = 300 L mol^{-1} s^{-1}
95% confidence interval: 998 ± 168 s^{-1}

→ **Very precise determination of k_{bb} in case of an acceptable experimental error**



σ = 600 L mol^{-1} s^{-1}
95% confidence interval: 959 ± 280 s^{-1}

→ **Even for a large experimental error, an accurate value for k_{bb} results**

Conclusions

- **Experimental data** of the full PLP-SEC trace are accurately described via the ***k*MC technique**
- The different **chain initiation** capability of the DMPA fragments is confirmed and related to the peak intensities of the PLP-SEC trace
- Importance of **short-long termination** is demonstrated, indicating the possible extraction of short-long termination kinetics from PLP experiments
- PLP-SEC data can be used to test the validity of models for **apparent termination rate coefficients** at low monomer conversions
- Variation of the solvent volume fraction in the low frequency range allows to accurately determine k_{bb}

References

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